Low-Temperature Heat Capacity Anomalies in Ordered and Disordered Phases of Normal and Deuterated Thiophene

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ABSTRACT: We measured the specific heat C_p of normal (C_4H_4S) and deuterated (C_4D_4S) thiophene in the temperature interval of $1 \leq T$, K ≤ 25. C_4H_4S exhibits a metastable phase II_2 and a stable phase V, both with frozen orientational disorder (OD), whereas C_4D_4S exhibits a metastable phase II_2, which is analogous to the OD phase II_2 of C_4H_4S and a fully ordered stable phase V. Our measurements demonstrate the existence of a large bump in the heat capacity of both stable and metastable C_4D_4S and C_4H_4S phases at temperatures of ∼10 K, which significantly departs from the expected Debye temperature behavior of $C_p \approx T^3$. This case study demonstrates that the identified low-temperature C_p anomaly, typically referred to as a "Boson-peak" in the context of glassy crystals, is not exclusive of disordered materials.
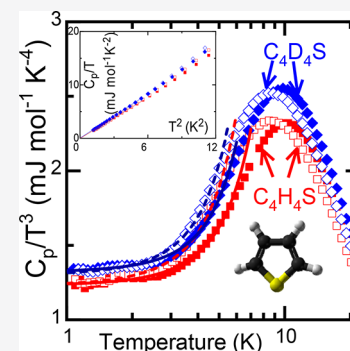
The search for the physical nature of low-temperature anomalies in the thermal properties of glasses and disordered crystals started ∼50 years ago.[1−4] Yet, to this day both structural and orientational glasses display anomalous properties that are still not fully understood. Among them, the physical origins and conditions of the existence of the so-called Boson peak (BP) stand out,[4−6] that is, a thermal anomaly leading to a heat capacity (C_p) maximum in the representation C_p/T^3 versus T. It is believed that the BP appears as a consequence of the excess of low-frequency states corresponding to a local maximum in the reduced vibrational density of states $(g(\omega)/\omega^2$ vs ω), which typically is attributed only to orientational or structural glasses.

The complex dynamics of the glass state is a consequence of low-energy excitations appearing in the vibrational density of states, $g(\omega)$, which in turn are manifested also in thermodynamic response functions like the specific heat.[7−9]

This letter aims at finding universal behaviors concerning well-ordered crystals, structural glasses, orientational glasses, and glassy crystals obtained by frozen statistical intrinsic disorder. The specific purpose of our study is to evidence some experimental facts that should help in disentangling the physical origin and nature of the BP associated with their heat capacity. With this purpose in mind, we performed highly accurate low-temperature C_p measurements on normal and deuterated thiophene, since these crystals harbor a unique diversity of fully ordered (FO) and orientationally disordered phases.

Thiophene is a planar heterocyclic aromatic compound (see inset in Figure 1) consisting of a planar five-membered ring with the S atom showing the direction of the molecular dipole. It displays a quasi-fivefold symmetry axis perpendicular to the
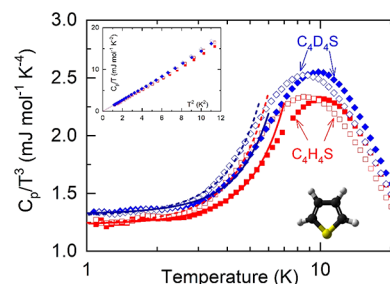
Figure 1. Debye-reduced specific heat data C_p/T^3 for the low-temperature OD metastable (empty symbols) and stable (full symbols) phases of C_4H_4S (red squares) and C_4D_4S (blue diamonds). Continuous lines are fits corresponding to eq 1. (upper inset) Specific heat data represented as C_p/T as a function of T^2 within the very low-temperature range (down to 4 K). (lower inset) Molecule of thiophene: C, black atoms; H or D, gray atoms; and S, yellow atom.

molecular plane. For both normal and deuterated materials, two similar phase sequences, one stable and one metastable, were broadly characterized, mainly structurally (see Scheme S1 in the Supporting Information). When cooled from the liquid phase ($T_m = 235$ K) an orientationally disordered (plastic) orthorhombic (*Cmca* space group) phase forms (I).[10,11] When further cooled and transitioned through some intermediate

Table 1. Heat Capacity Coefficients (eq 1) and Characteristic Temperatures[a]

material	phase (state)	C_1 mJ K^{-2} mol^{-1}	C_3 mJ K^{-4} mol^{-1}	$C_5 \times 10^3$ mJ K^{-6} mol^{-1}	$C_7 \times 10^5$ mJ K^{-8} mol^{-1}	T_{max} K	Θ_D K	T_g K
C_4H_4S	V(OD)	0 ± 0.05	1.23 ± 0.06	9.8 ± 1	23.7 ± 3	10.0	116.7	41.7
	II$_2$(OD)	0 ± 0.05	1.23 ± 0.06	14.6 ± 2	48.0 ± 7	8.4	116.7	36.9
C_4D_4S	V(FO)	0 ± 0.05	1.32 ± 0.06	9.9 ± 2	39.7 ± 7	10.0	114.0	
	II$_2$(OD)	0 ± 0.05	1.30 ± 0.06	15.0 ± 2	59.9 ± 7	8.5	114.6	39.1

[a]θ_D, Debye temperature obtained from C_3 coefficient ($\theta_D^3 = 12\pi^4 R/(5 \cdot C_3)$); T_{max} is the temperature at which C_p/T^3 exhibits the maximum of the specific heat, and glass transition temperature (T_g) for the low-temperature stable (S) and metastable (M) phases of normal and deuterated thiophene. OD is orientational disordered; FO is fully ordered.

phases (II and II$_1$), the phase II$_2$ is finally formed and remains metastable down to the lowest temperature that was measured (1 K for C_4D_4S and 14 K for C_4H_4S).[12,13] Despite both II$_1$ and II$_2$ phases being metastable, a reversible first-order phase transition at 90.7 K from II$_2$ to II$_1$ is found when heated. Further heating from phase II$_1$ and annealing at ~160 K results in the formation of the orthorhombic stable phase III (space group *Pnma*). When phase III is cooled, phase IV, an incommensurate superstructure of phase III (*Pbnm* space group), and phase V, a superstructure of phase III corresponding to a doubling of the *a* parameter, are sequentially and reversibly found. With regard to the orientational disorder, phase I displays 20 equiprobable molecular orientations, whereas 10 are exhibited in phases II (as well as II$_1$ and II$_2$) and III for both normal and deuterated samples. In addition to some subtle differences in the transition temperatures, the main, interesting, and distinguishing experimental difference between the normal and deuterated thiophenes concerns the dynamical disorder of the low-temperature phase V.[11,13,14] For both materials, the metastable sequence providing the disordered phase II$_2$ at a low temperature, a glass transition temperature of 36.9 K, and, coherently, a residual entropy extrapolated at 0 K of 1.48 ± 0.9 J·K^{-1}·mol^{-1} [13] were found, reinforcing the orientational glassy character of this metastable phase previously determined through X-ray and neutron diffraction.[11,14,15] With regard to the stable sequence, the low-temperature phase V shows up the greatest difference: For C_4H_4S, phase V retains the orientational disorder of phase III, giving rise to an orientational glassy phase V (called V$_g$) with a glass transition temperature of 41.7 K,[13] whereas phase V of C_4D_4S was irrefutably found to be a fully ordered phase.[12]

The orientational disorder of the C_4H_4S phases was also confirmed through dielectric spectroscopy.[16] However, experimental thermal conductivity studies on the low-temperature orientational disorder (OD) phases of normal thiophene show a temperature dependence that is typical of ordered crystals.[17,18]

As a summary, the low-temperature phase domain of heterocyclic aromatic molecular crystalline thiophene can display different orientational glasses in which a disorder (or order) level can be operated via a substitution of protons by deuterons. Thus, at a low temperature, two phases can be found for each C_4H_4S and C_4D_4S material: the metastable (plastic) phase II$_2$ and the stable phase V for C_4H_4S, both with frozen orientational disorder below the respective glass transitions (at 36.9 and 41.7 K, respectively), and the metastable (plastic) phase II$_2$ (exhibiting the same properties as OD phase II$_2$ of C_4H_4S) and the FO phase V for C_4D_4S.

Measurements of the specific heat, C_p, from 1 K up to the melting point were performed for both the metastable and

stable phases of C_4H_4S and C_4D_4S. In particular, for samples C_4H_4S (17.2017 mg) and C_4D_4S (20.3136 mg) the measurements were carried out with a Quantum Design relaxation-type calorimeter PPMS employing a ^{3}He probe in the temperature interval of $1 \leq T$, K ≤ 20. In addition, specific heat measurements for the sample C_4D_4S (0.31618 g) were performed with a laboratory-made adiabatic calorimeter from 10 to 300 K.[19] Resolutions of the measurements are ca. 0.3% for the relaxation calorimetry and ca. 0.2% for the adiabatic calorimetry. The results presented next will focus on the low-temperature interval of $1 \leq T$, K ≤ 25.

Figure 1 shows the experimental specific heat along with the typical Debye representation, C_p/T^3, expressed as a function of temperature for the metastable (plastic) and stable phases of C_4H_4S and C_4D_4S. Figure 1 evidences that, independently of whether the phase is OD or FO, all the specific heat curves exhibit a maximum in the C_p/T^3 representation. Despite the similarity of the maximum temperature values, the maximum occurs at slightly lower temperatures for the OD II$_2$ phases than the V phases. In addition, deuteration leads to an increase in the C_p maximum as well as in the Debye contribution to C_p (C_3), the latter being independent of the ordering character of the phase.

According to its most canonical low-temperature approximation, the specific heat of a crystal can be expressed as a function of temperature as

$$C_p = C_1 \cdot T + C_3 \cdot T^3 + C_5 \cdot T^5 + C_7 \cdot T^7 + \dots \quad (1)$$

where the C_1 term accounts for possible "two-level state" (TLS) tunneling effects,[20,21] C_3 accounts for the well-known contribution from acoustic modes (i.e., the Debye model), C_5 accounts for the BP, which can be explained based on different models, and C_7 and additional higher-order terms account for high-temperature features.[22] Note that this low-temperature approximation applies to temperatures below T_{max}, at which C_p/T^3 exhibits its maximum.

Within the temperature range of the measurements ($T \geq 1$ K), Figure 1 does not reveal one of the most common and distinctive fingerprints of glasses, the linear term for C_p at very low temperatures (C_1 in eq 1), for the studied ordered and disordered crystals. To confirm the lack of such a term, we represent C_p/T versus T^2 for temperatures lower than 4 K in the inset of Figure 1. On the contrary, our experimental results unambiguously show the existence of a bump (BP) in the glassy crystalline states (orientationally disordered metastable phases, II$_2$, for both C_4H_4S and C_4D_4S) as well as in the disordered stable phase V of C_4H_4S. Such a thermal anomaly is a typical feature of OD phases[23] as well as crystalline phases with occupational disorder, even for weakly bonded molecular crystals.[23−27] A Boson-like peak also appears in the fully ordered stable low-temperature phase V of C_4D_4S with similar

intensity to that of phase II, which from the canonical knowledge could be ascribed to the first van Hove singularity. Nevertheless, its characteristic temperature coincides with that of the orientational glassy phase V of C_4H_4S (i.e., 10.0 K, see Table 1), and it is also very close to those observed for OD phases II_2.

For perfectly ordered crystals, like noble gases, the C_5 term accounts for the normal dispersion of the acoustic branches of the crystal,[28] that is, a kind of forerunner of the bump in normalized heat capacity, which is associated with the first van Hove singularity in the density of vibrational states. Meanwhile, the nature of the C_5 heat capacity term for disordered solids is still under debate, and various theoretical physical interpretations have been proposed for it. Examples include the existence of additional soft anharmonic modes,[29] the presence of heterogeneities in the elastic constants of the continuous medium,[30−32] the smearing out of the lowest van Hove singularity appearing in the crystalline counterpart,[33,34] and the stack of transverse excitations (at frequencies around the BP).[5]

Interestingly, a recent model proposed by Baggioli and Zaccone assembles the explanation of the BP from a unified description regardless of the ordering of the system.[35−37] This model proposes, as suggested in a recent experimental work,[38] that the BP in $g(\omega)$ can simply appear by the piling up of low-energy optical modes provided that their energy is close to that of the acoustic modes at the reciprocal space points of the Brillouin zone boundary. For sufficiently low energies of the first optical mode at the Brillouin zone center (ω_o), that is, close to the energy of the acoustic modes, the magnitude of the BP is reinforced, whereas for large ω_o the contribution to the BP vanishes, regardless the order of the system. Moreover, the model accounts also for the C_1 linear term in eq 1 as due to the damping of the optical modes (that can be also related to anharmonicity for perfectly ordered crystals). For low values of the damping term, C_1 is decreased, whereas the intensity of the BP is enhanced.

It is worth noting that, since there is not a quantum theory for the dynamics of glasses and disordered systems, the theoretical models listed above are mainly phenomenological and provide only a qualitative description of the low-temperature anomalies observed for their specific heat.

The results in Figure 1 (see inset) clearly reveal the nonexistence of the upturn of the curve at the lowest temperatures (∼1 K), which, according to the previous model, would mean that, whatever the phase (ordered or disordered) and compound (normal or deuterated), the damping of the optical modes is negligible. Nevertheless, our first-principles calculations (explained below) show a strong anharmonic character of the ordered phase V of C_4D_4S, which suggests that anharmonicity cannot be the only cause for the appearance of the TLS regime (at least not in ordered crystals, as it is predicted by the Baggioli and Zaccone model.[35−37]). Nevertheless, we cannot rule out the possibility that the linear contribution to C_p appears at temperatures below 1 K.

According to the values of the C_3 coefficient, which is related to the elastic properties of the crystal, the Debye temperatures Θ_D of normal and deuterated thiophenes are only slightly different. Specifically, for both the low-temperature phases V and II_2, $\Theta_D(C_4D_4S)$ is less than $\Theta_D(C_4H_4S)$ (see Table 1). Because the Debye (elastic) temperature, proportional to the speed of sound, is mainly determined by the speed of transverse acoustic modes (v_T), the small differences between the normal and deuterated Debye temperatures (for both

stable phases V and metastable phases II_2) can be accounted for by the difference in their densities (∼4% according to refs 12 and 14), which consistently should be accompanied by a similar difference in the shear modulus ($v_T^2 = \mu/\rho$). Moreover, although the higher molecular weight of deuterated thiophene should lead to a lower temperature for the maximum of C_p/T^3 versus T,[38] Figure 1 and Table 1 evidence that the corresponding T_{max} values are virtually the same for normal and deuterated samples when comparing the respective phases II_2 (8.4−8.5 K) and V (10.0 K). Accordingly, the experimental similarity between the excess in the density of vibrational states of the orientational glasses (phases II_2 of both normal and deuterated, as well as disordered phase V of normal compound) cannot be attributed to the elastic differences (acoustic modes) between different crystalline phases, but univocally to the existence of additional (optical) modes appearing at energies around the BP. This fact is confirmed by first-principles calculations of the density of vibrational states for the well-ordered phase V of C_4D_4S using ab initio molecular dynamics (AIMD) simulations based on density functional theory (DFT) (see the Supporting Information for details); we note that, even for the FO phase of deuterated thiophene, standard harmonic DFT approaches cannot provide physically meaningful results due to the inherently high anharmonicity of the system.

In particular, on the one hand, the phonon frequency spectrum calculated with harmonic DFT methods for the ordered phase V of C_4D_4S (not shown here) displayed a large number of imaginary phonon modes. On the other hand, AIMD calculations, which fully can take into account the anharmonicity of the system,[39] rendered a well-behaved density of vibrational states (i.e., all phonon frequencies were real) for the ordered phase V of C_4D_4S. Figure 2 shows the
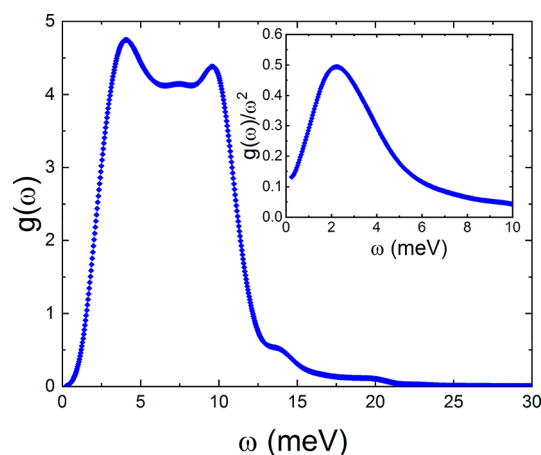

Figure 2. Low-energy part of the vibrational density of state ($g(\omega)$) expressed as a function of the energy (ω) for the low-temperature FO phase V of C_4D_4S. (inset) Reduced density of states ($g(\omega)/\omega^2$ vs ω). Results were calculated theoretically by means of first-principles AIMD approaches based on DFT.

calculated $g(\omega)$ expressed as a function of ω as well as the reduced vibrational density of states $g(\omega)/\omega^2$ (inset Figure 2), which clearly evidence the BP for the FO phase.

The C_v/T^3 curve that results from the AIMD calculations is qualitatively in good agreement with the experimental observations. In particular, a bump, that is, a BP, appears at low temperatures, and the characteristic signature of the TLS shows

regime is missing. The temperature at which the BP appears in the calculations (~7 K), however, is slightly lower than the one observed in the experiments (10 K). The quantitative disagreement between our calculations and experiments is reasonable after considering that likely thermal expansion and quantum effects have been neglected in the theoretical results. A comparison between the calculated specific heat (at constant volume C_v) and experimental C_p values is shown in Figure 3, where the specific heat curves were referred to their Debye values (C_3 coefficient) and normalized.
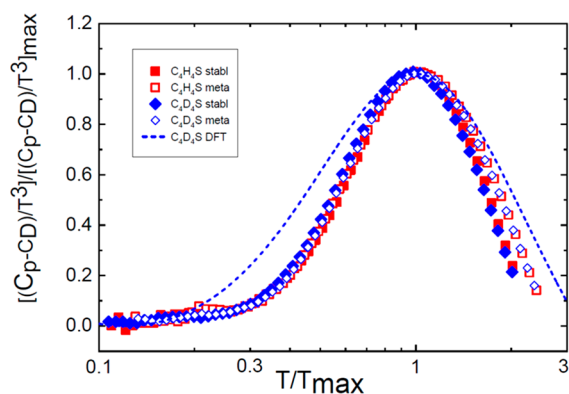

Figure 3. Specific-heat data normalized with respect to Debye values (C_D, i.e., C_3 coefficient for the experimental data) scaled to the height $[(C_p - C_D)/T^3)]/[(C_p - C_D)/T^3)]_{max}$ as a function of the temperature normalized to the position of the peak. Dashed line depicts the calculated values (for C_v), whereas symbols (as in Figure 1) concern the experimental values.

From the first derivative of $g(\omega)$ with respect to ω, we deduce that, in the regime of low vibrational frequencies ($\omega <$ 5 meV), the maximum variation of $g(\omega)$ with respect to ω occurs at ~2 meV. We tentatively ascribe this energy to the lowest optical phonon branches appearing in C_4D_4S (FO phase V), which coincides with the frequency at which the function $g(\omega)/\omega^2$ is maximum (inset, Figure 2).

As a consequence, optical phonons within the energy range of strongly dispersive phonon branches indiscernibly contribute to the so-called BP; thus, anomalies in the C_p/T^3 versus T representation (or alternatively in $g(\omega)/\omega^2$ versus ω) cannot account for the glassy or crystalline character of a given phase. In other words, the so-called BP reflects the features of the crystal dispersion and appears as a consequence of the characteristic acoustic and optical phonon branches of each crystalline phase in such a way that disorder can only modify slightly the density of vibrational states, but it does not seem to be at the origin of the phenomenon.[40]

In addition, the linear term in the heat capacity (not attributed to conduction electrons), repeatedly considered as the fingerprint of glasses, does not seem to be a necessary condition for glasses and, contrary to what has been reported in a recent theoretical study,[32] it does not seem to be a consequence of the anharmonicity of the system (at least, within the temperature regime analyzed in this work).

To generalize the above conclusion, in Figure 4 we represent the C_p/T^3 function normalized by its Debye contribution and represented as a function of T/T_{max} for a wide range of solids including atomic (Ar) or diatomic (p-H$_2$), completely ordered crystals (glycerol, deuterated ethanol (D-ethanol), deuterated thiophene, and cristobalite and coesite SiO$_2$), weakly
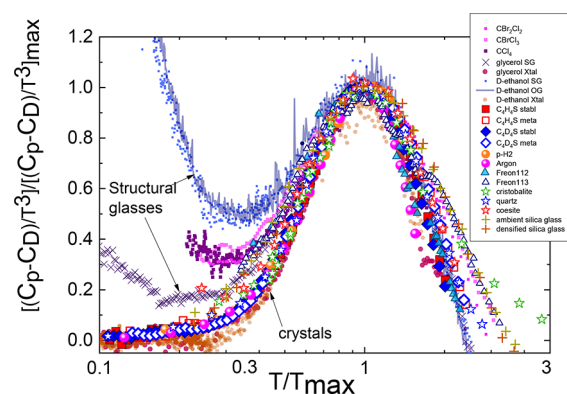
Figure 4. Specific-heat data referred to Debye values (C_D), scaled to the height $[(C_p - C_D)/T^3)]/[(C_p - C_D)/T^3)]_{max}$ as a function of the position of the peak for different materials: Low-temperature phase of CCl_4 (black empty squares), $CBrCl_3$ (full red circles), and CBr_2Cl_2 (blue empty circles) halomethanes;[38] structural glasses as glycerol[41] (pink line), deuterated ethanol (green dots), orientational glass of deuterated ethanol[42] (continuous green line), freon112 (blue triangles), and freon113 (empty triangles);[24−27] ordered crystalline phases of glycerol[41] (pink circles), ethanol[42] (green circles); stable and metastable phases of normal (full and empty black squares) and deuterated (full and empty black diamonds) of thiophene and well-known materials as p-hydrogen[43] (full orange circles), argon[44] (full blue circles) and SiO$_2$ (glass state as well as the ordered cristobalite and coesite phases).[34]

disordered molecular crystals (CCl_4, $CBrCl_3$, CBr_2Cl_2), orientational glasses (D-ethanol, normal and deuterated thiophenes, freon112, and freon113), and completely disordered molecular structural glasses (D-ethanol, glycerol, SiO$_2$). It is noteworthy that, in the case of simple crystals like Ar and p-H$_2$, T_{max} corresponds to the first feature of the van Hove singularity in the density of vibrational states, which is caused by acoustic vibrational excitations with transverse polarization; in the case of completely ordered crystals, the T_{max} corresponds to the low-lying optical branch, and in the case of loose crystals and glasses, the T_{max} is the maximum temperature of the so-called BP.

It is clearly seen that the scaled excess heat capacity of distinct types of solids is characterized by a same trend with universal behavior, both on the left and right of its maximum. A deviation from such a universal behavior appears in some disordered crystal and glasses, when the linear contribution of heat capacity begins to manifest and dominate under a decreasing temperature.[45−50]

We emphasize that the paradigm of the BP will likely find an answer (not provided in this paper) through the study of partially and weakly disordered systems. While structural (canonical) glasses can be described by means of phonon-like optical quasi-localized modes and phonon-like acoustic modes in a pseudo-Brillouin zone, partially and weakly disordered systems with long-range translational order and orientational disorder display genuine acoustic and optical phonons in a real Brillouin zone, which should provide evident clues for the correct answer.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c00289.

Stable and metastable phase transitions, discussion of density functional theory calculations, additional references (PDF)

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Notes

The authors declare no competing financial interest.

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